ETHANOL DRY REFORMING FOR H_2 PRODUCTION OVER LANTHANIDE-GROUP PROMOTED Co/Al_2O_3 CATALYSTS

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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JUNE 2015

ABSTRACT

This paper presents the studies of the La-group promoter addition effects and their performances. Three different catalysts are synthesized with addition of different promoters supported by alumina. The catalysts are synthesized by using the wet impregnation process, which involved dissolving and mixing specific calculated amount of nitrate salts and calcined alumina in distilled water. The solutions are then stirred for 3 consecutive hours before they are dried in the oven for 12hrs. Lastly, the catalysts are calcined in a furnace at 1023K for 5 consecutive hours to remove remaining water content and nitrates. The calcined and uncalcined catalysts were collected for catalyst characterization analysis which involved, Thermalgrametric Analysis (TGA), Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) and X-ray Diffraction Analysis (XRD). Calcined unreduced catalysts were used for ethanol dry reforming syngas production reaction runs at conditions of temperature 973K, pressure 1 atm, and 1:1 C_2H_5OH to CO_2 ratio. The content of the produced syngas were analyzed using gas chromatography, and the results were compared between the catalysts for their performances.

XRD analysis showed that the second metal promotion did not affect the original structure of catalyst. The SEM analysis indicates addition of cerium and lanthanum as promoters affected the morphology of the catalyst by altering the surface texture by introducing flakes to the molecular surface of the promoted catalysts. Addition of La-group promoters is capable to provide stable catalytic performance and slightly improved C_2H_5OH and CH_4 conversion into syngas mixture of H_2 and CO when compare to non-promoted cobalt catalyst. The promoter addition decreases/slow-down the process of carbon decomposition on the catalysts' surfaces in the order; La > Ce > non-promoted Co/Al_2O_3 catalysts together boosts up the production of H_2 and CO gas in term of production rate, yield and also selectivity. The production output H_2:CO ratio is very suitable for downstream production such as Fischer–Tropsch synthesis. The trend of CH_4:CO ratio suggests catalytic reforming of methane from ethanol decomposition occurrence, where methane was converted into syngas mixture of CO and H_2. The overall performances of catalysts increased by the promotion order, La > Ce > non-promoted Co/Al_2O_3 catalysts.

Key words: ethanol, dry reforming, La-group promoter, syngas, characterization, Fischer–Tropsch synthesis, conversion, yield, selectivity, increased performances

TABLE OF CONTENTS

List of Figures

List of Tables

1 INTRODUCTION

1.1 Motivation and statement of problem

Energy is one of the major issues that we are facing in this era of modernisation. The world energy demand is increasing exponentially as the technologies are evolving and getting generalized globally. This can be seen by the common example of the comparison in the local society around us in nowadays and the society in past decade. In the 20th century, where cars were once considered a luxurious item which can only possess by the rich and high social status person, however it has became a need for almost everyone who is working in the urban cities. These days tons of vehicles can be spotted everyday on the road, this illustrating the increasing high demand of energy in term of gasoline required to drive the vehicles in motion. Aside from the view of the increasing energy demand from gasoline, by looking at the electricity demand chart from TNB Malaysia also gives a solid prove on the increasing local energy demand. [1]

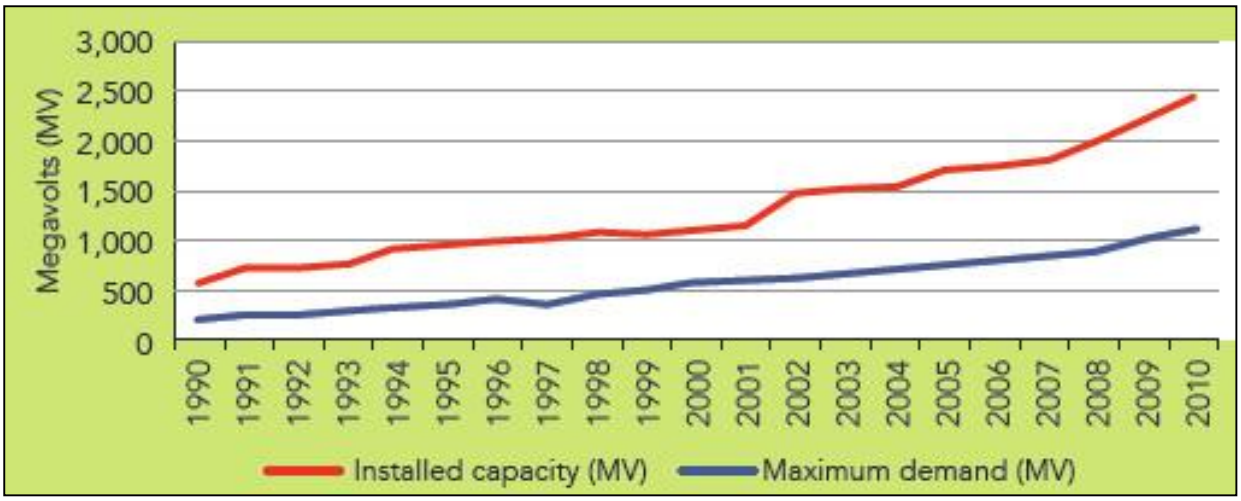

Figure 1-1 Installed capacity and maximum demand of electricity in Peninsular Malaysia by TNB

With the exponentially increase trend like this, there might be possibly that the running out of the crude oil reserves to be happened. The debate is nevertheless important because if without sufficient investment in demand of substitute sources of energy, a decline in the global production of conventional crude oil in the future could have major economic impacts. [2] Recently, the need to reduce the dependence on petroleum as feedstock and the continuous increase of natural gas proven reserves has generated interest in the extensive use of this natural resource. Unfortunately, the majority of world gas reserves are located either in small fields or in remote regions which cannot be monetized using conventional technologies (pipelines or LNG). In addition, some stranded gas reserves are associated to oil. The increase of environmental restrictions to gas flaring or ventilation makes difficult the development of these fields. The conversion of natural gas to liquid fuels, the so-called gas-to-liquids (GTL) technology, is a promising alternative to the monetization of stranded gas reserves and to fulfil the environmental restrictions. [3]

Synthesis gas is a mixture of hydrogen and carbon monoxide with the ratio varying depending on the desired product. The synthesis gas also usually contains inert compounds such as argon, methane, nitrogen, carbon dioxide, and so forth. Synthesis gas can be made in a variety of devices, but is almost always made by reforming natural gas. [4] Besides, hydrogen is also an alternative energy source that can be converted to electricity in a fuel cell device. [5,6] There are several ways in producing synthesis gas, like partial oxidation, steam reforming and autothermal reforming. However as compared to other syngas production processes, ethanol dry reforming (DRE) reaction is industrially advantageous since it yields syngas with H2/CO product ratio close to unity which is more suitable for liquid hydrocarbon production via Fischer–Tropsch synthesis and in the production of oxygenated compounds. The main drawback of DRE is its endothermic nature which requires fairly high temperatures to achieve high conversion values. This severe operating condition could cause catalyst deactivation due to accumulation of coke over catalyst surface and/or sintering of the active metal particles. Generally, the catalysts used for the DRE are categorized into two groups: supported noble metals (Pt, Pd, Rh, Ru) and non-noble transition metals (Ni, Co, Fe). [7]

Study on the catalyst development of this reaction has been focused on screening a new catalyst to reach higher activity and better stability toward sintering, carbon deposition (coking), metal oxidation, and forming of inactive chemical species. Recently, although not a focus of attention, it has been revealed that the supported cobalt catalyst shows considerable activity for dry reforming of ethanol process. Even though the catalytic performance, such as activity is neither superior to nickel nor to the noble metal catalyst, study on the supported

cobalt catalysts were also reported to find out the better catalytic performance. It is also probable that the mechanism of carbon deposition on cobalt metal is different from that on nickel metal. Cobalt catalyst, especially over silica and alumina supports, is also reported to have a good stability against temperature changes. These results suggest that cobalt catalyst is a potential alternative among non-noble metal catalysts with a small amount of carbon deposition. [8]

1.2 Objectives

The following are the objectives of this research:

- To synthesize and characterize the physicochemical properties of Lanthanide group promoted Cobalt catalysts, 3%Ce-10%Co/Al_2O_3, 3%La-10%Co/Al_2O_3 and 10%Co/Al_2O_3.
- To evaluate performance of dry reforming of ethanol by using different promoters on unreduced catalyst.

1.3 Scope of this research

The following are the scope of this research:

i) To fabricate the Lanthanide group promoted catalysts, 3%Ce-10%Co/Al_2O_3, 3%La-10%Co/Al_2O_3 from $Co(NO_3)_2$•$6H_2O$, $Ce(NO_3)_3$•$6H_2O$ and $La(NO_3)_3$•$6H_2O$ through the application of impregnation followed by drying process at temperature of 110 ˚C for 24 hours.

ii) To characterize the synthesized catalyst by using following advanced techniques like X-ray Diffraction Measurement (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).

iii) To test catalytic behavior of unreduced catalysts with different catalyst promoters for CO_2 (or dry) reforming process in order to locate ideal process settings for top performances.

1.4 Main contribution of this work

Carbon dioxide (CO_2) has been identified as the most significant greenhouse gas arising from anthropogenic activities. It is of great importance to reduce anthropogenic CO_2 emissions in order to counteract global warming. One such method, which is presently being extensively investigated, is the sequestration of CO_2 produced by concentrated sources (such as industrial plants and power stations). However, no one can be sure of the potential influence of CO_2 buried on the ecosystem in the long term. Conversion of CO_2 instead of its sequestration is presently being explored as one potential alternative solution. Production of useful value-added products (chemicals products, fuels …) by dry reforming of ethanol appears to be an interesting method. DRE produces an equimolar synthesis gas (syngas) which is a mixture of hydrogen (H_2) and carbon monoxide (CO), from carbon dioxide and ethanol (C_2H_5OH), according to equation below:

$$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2$$

Today, the industrial application of ethanol dry reforming is limited. Indeed, there are only two industrial processes to produce some syngas (H_2 and CO). Similarly, there are only two pilot plants for the production of more interesting products such as: hydrogen (H_2) and liquid synthetic motor fuels (naphtha (C_8H_{18}-$C_{12}H_{26}$), kerosene ($C_{11}H_{24}$-$C_{13}H_{28}$) and gasoline (C_5H_{12}-$C_{12}H_{26}$).

Undeniably, dry reforming can be viably used as a method of CO_2 mitigation for the production of hydrogen or of synthetic fuels. This work assesses whether monometallic catalyst can be replaced by promoted catalyst and used in dry reforming reaction to give a promising conversion of syngas from CO_2 utilisation. First, a comparison between the monometallic catalystt and lanthanum group promoted catalyst is performed as well as a study of the production of hydrogen from the dry reforming of methane. Furthermore, a thermodynamic analysis is carried out by the method of equilibrium constants defining the thermodynamic limit and the optimum conditions.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 shows the motivations, objectives and scopes of this project. Current problems in energy field are described and solutions to the problem are suggested. Scopes of this project include the works and experiments that are to be carried out for the whole project. Main contribution of this work which covers the essential reaction in ethanol reforming technology also shown in this part of the report.

Chapter 2 provides a description of the applications of catalytic steam reforming, CO_2 reforming and catalytic partial oxidation. A general description on the flow characteristics of the system, as well as the advantages and disadvantages are presented. This chapter also provides a brief discussion of different types of catalyst, mentioning their applications and limitations for reforming process as well as the catalyst deactivation. A summary of the previous experimental work of CO_2 reforming is also presented.

Chapter 3 gives a flow chart of preparing the monometallic catalyst and lanthanum group metal promoted catalyst by using wetness impregnation method, followed by mixing slurry and lastly drying and calcination process. In the preparation of lanthanum group metal promoted catalyst section, multiple impregnation technique is selected instead of co-impregnation in order to ensure the desired compositions of metals are loaded on the alumina support respectively. The other sections give detailed explanations about the preparation procedures and precautions.

Chapter 4 is devoted to the results and discussions of this project. In this chapter, the detailed descriptions about the result of characterization by using advanced technologies as well as the catalysts' performances in dry reforming reaction are discussed.

2 LITERATURE REVIEW

2.1 Overview

This chapter present a detailed description of alternative technologies in producing syngas, advantages and disadvantages as well as the challenges nowadays towards their performances. Furthermore, other sections include a brief list of noble metal used in catalytic reaction, description of challenges or problems encountered by catalysts during reaction

2.2 Introduction

In the syngas production processes such as steam reforming and partial oxidation, the dry reforming of carbon dioxide is becoming the most promising technology since it produces syngas with the H_2/CO ratio close to unity which is suitable for methanol and other Fischer-Tropsch syntheses. The dry reforming of ethanol is typically followed by the reverse water–gas shift reaction and the formation of undesired carbon deposition produced through methane decomposition and the Boudouard's reaction. [8]

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H_{298} = 46.1 kJ/mol \qquad (1)$$

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H_{298} = 74.9\ kJ/mol \qquad (2)$$

$$2CO \rightarrow CO_2 + C \qquad \Delta H_{298} = -172.5 kJ/mol \qquad (3)$$

At the reaction temperature, ethanol may decompose into methane according to the following reaction: [46]

$$C_2H_5OH + CO_2 \leftrightarrow CH_4 + 2CO + H_2 \qquad \Delta H_{298} = 49\ kJ/mol \qquad (4)$$

Study on the catalyst development of this reaction has been focused on screening a new catalyst to reach higher activity and better stability toward sintering, carbon deposition (coking), metal oxidation, and forming of inactive chemical species. Numerous scientific publications reported that all members of group VIII transition metals with the exception of osmium especially Ni, Ru, Rh, Pd, Ir, and Pt perform an activity to this reaction. Among these metals, noble metals such as ruthenium and rhodium have been shown to be the most active and resistant from carbon deposition. However, based on economical view, upscale toward industrial level of noble metals is not suitable considering their high cost and restricted availability. [13]

On the other hand, supported nickel is commonly studied because of its low cost and better availability. Supported nickel catalyst has a major problem such as carbon deposition which possibly forms on the catalyst surface and/or on the tubes of the reactor and lead to deactivation of the catalyst and/or a plugging of the tubes. Because of that reason, it is impossible to avoid carbon formation under low or unity CO2/CH4 ratios using nickel catalyst.[14]

Recently, although not a focus of attention, it has been revealed that the supported cobalt catalyst shows considerable activity for dry reforming of methane process [12]. Even though the catalytic performance, such as activity is neither superior to nickel nor to the noble metal catalyst, study on the supported cobalt catalysts were also reported to find out the better catalytic performance [11]. It is also probable that the mechanism of carbon deposition on cobalt metal is different from that on nickel metal. Cobalt catalyst, especially over silica and alumina supports, is also reported to have a good stability against temperature changes [11]. These results suggest that cobalt catalyst is a potential alternative among non-noble metal catalysts with a small amount of carbon deposition.

In case of non-noble metal catalyst, the catalyst deactivation and carbon deposition (coking) have become the main constraints in the development of catalyst. Gadalla and Sommer indicated that the deactivation of catalyst may be influenced by carbon deposition, metal sintering, or formation of inactive species during the reforming reaction, while Takanabe added metal oxidation as the other factor [15].

The thermodynamic calculations of two side reactions causing carbon deposition in catalyst, namely methane decomposition and the Boudouard's reaction, have been done using Gibbs free energy calculation [9]. The methane cracking reaction would proceed in the reaction temperature above 553 ^{o}C while the Boudouard reactions could occur in the temperature below 700 ^{o}C. In the range 553–700 ^{o}C the formation of carbon deposition most likely takes place by both reactions.

The limiting temperature curve for carbon deposition for different values of the CO_2/CH_4 ratio and total pressures are studied via thermodynamic calculation (Fig. 1.1) [15]. The temperature operation above curve indicated in Fig. 1.1 should be applied to avoid carbon deposition. For the same feed ratio, the temperature limit for carbon deposition increases as the pressure increases. Additionally at a given pressure the temperature limit increases as the

CO2/CH4 feed ratio decreases. This means that using excess CO2 in the feed may avoid carbon formation at lower temperatures.

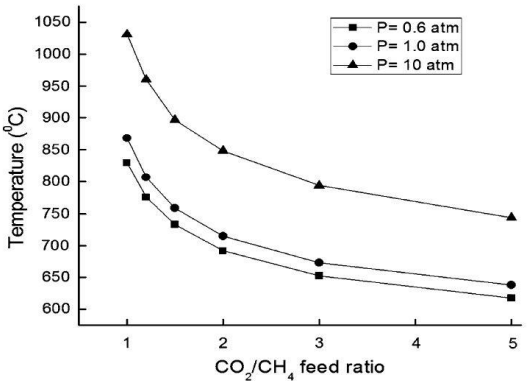

Figure 2-1 Effect of feed ratio on the temperature below which carbon deposits at various pressures [15]

The methane decomposition on the active metal site becomes one of the most important paths in dry reforming reaction since it generates the reactive carbon species then are oxidized to CO by the oxygen-containing species that originate from CO2 activation [16–18]. No carbon deposition would occur when the reactions between these methane decomposition and carbon oxidation on the surface of the catalyst are kinetically balanced. The carbon deposition will occur if the relative rates of the generation of carbon species are lower than the latter mechanism. Furthermore, the relatively large active metal sites to the support likely stimulate a carbon deposition. The balance between reduction and oxidation can strongly be reached to provide better catalytic performance by selection of optimum cobalt loading.

In another case, if the oxidation of carbon species occurs at relatively higher rate than the methane decomposition, as in the case of very low number of active metal site in basic supported catalyst, the oxygen species will oxidize active metal site to form inactive species. The deactivation caused by the metal oxidation during the CH4/CO2 reaction has also been reported for NiMgO solid solution, [19] molybdenum carbide [20] Co/c-Al2O3 [21] and Co/TiO2 [22].

2.3 Reaction Mechanism

The occurrence of dry reforming process is following the decomposition of ethanol into methane, carbon monoxide and hydrogen gases. [46] There are many mechanism models of dry reforming proposed since 1967, where the first reaction mechanism was proposed by Bodrov and Apel'baum. [28] However, only one of the lastest and simplistic mechanism will be discussed here, which is the model suggested by Mark and Maier [29] and Lercher et al. [30]:

$$CH_4 + * \rightarrow C* + 2H_2 \quad (5)$$

$$CO_2 + 2* \leftrightarrow CO* + O* \quad (6)$$

$$C* + O* \leftrightarrow CO* + * \quad (7)$$

$$2CO* \leftrightarrow 2CO + 2* \quad (8)$$

In this proposed sequence of reactions, some of which are not elementary, * denotes an active site on the catalyst surface, → denotes a slower irreversible reaction, and ↔ denotes a reversible reaction. This sequence of steps was derived from a series of pulsed adsorption experiments in which CH_4 was shown to decompose stoichiometrically to carbon and H_2, and CO_2 was found to react stoichiometrically with surface carbon to yield CO [29]. However, pulsed CH_4 adsorption experiments can yield primarily atomic carbon, the most thermodynamically stable species [31], whereas transient in situ experiments can identify CH_x species as reactive intermediates during CO_2 reforming of CH_4, as mentioned previously. Furthermore, Osaki et al. have shown that the Turnover-Frequency for CO_2 reacting with surface carbon resulting from CH_4 decomposition are much lower than Turnover-Frequencies for CO_2 reforming of CH_4 over supported Ni catalysts [32]. These results do not support the alternate mechanism proposed by Mark and Maier [29] and Lercher et al. [30].

On the other hand, a mechanism model is proposed by M.C.J. Bradford and M.A. Vannice after studying several researches in the reaction mechanism of CO_2 reforming by other researchers like Ceyer et al., van Santen and Neurock, Luntz and Harris, Beebe et al., Trevor et al. and etc. in term of metal surface: [13]

$CH_4 + 2M \leftrightarrow CH_3\text{-}M + H\text{-}M$ (9)

$CH\text{-}M + 2M \leftrightarrow CH_2\text{-}M_2 + H\text{-}M$ (10)

$CH_2\text{-}M_2 + 2M \leftrightarrow CH\text{-}M_3 + H\text{-}M$ (11)

$CH\text{-}M_3 + 2M \leftrightarrow C\text{-}M4 + H\text{-}M$ (12)

where M_n is an ensemble of n-surface metal atoms. This requirement demonstrates the high probability of structure sensitivity in the formation of surface carbon because of the large ensemble of metal atoms needed. Note that the stoichiometry of reaction is valid provided that the metal surface in question has fourfold sites, such as Pt. CH_x fragments are preferentially located at a site on the metal surface which completes its tetravalency; that is, the stepwise decomposition of CH_4 into CH_x fragments on a metal surface requires the concomitant occupation of higher coordination sites. [13] CH_x species on transition metal surfaces have been detected using both transient CH_4/D_2 and CD_4/H_2 exchange [33,34] and deuteration of preadsorbed CH_4 [35]. However, simple model calculations based on $–CH_x$ bond strengths on metal surfaces show that the distribution of CH_x species observed with the latter technique may be controlled by thermodynamic equilibrium and not kinetics [36].

2.4 Reaction Kinetics

A wide range of activation energies, E_i, has been reported (i.e., values for CH_4 disappearance vary from 7 to 86 kcal/mol). According to Bradford, that in practice a heterogeneous catalyst may have a distribution of catalytic active sites with different intrinsic activation barriers for the chemical reaction of interest. Consequently, it is interesting that the distribution of apparent activation energies reported for CO_2 reforming of CH_4 shows that 14 ± 1 kcal/mol is the most frequently observed, a value which coincides with activation energies of 13.3 ± 1.5 and 12.6 ± 1.2 kcal/mol for CH_4 dissociation on Ni(110) and Ni(111), respectively [13]. Besides, Bradford also studied and reviewed several analytical data whereby they illustrate that $E_{H2} \geq E_{CO}$ and if the data for SiO_2-supported catalysts are not considered, CO_2 inhibits H_2 formation. These two observations suggest that the apparent E values for CO and H2 are strongly influenced by the reaction of CO_2 with H_2, presumably via the RWGS reaction. In addition, apparent E_i values can be strongly influenced by the space velocity (SV) that as

the SV increases, CH_4 and CO_2 conversion decreases along with the residence time, and the influence of the first part of the reverse reaction (i.e., CO hydrogenation to CH_4) becomes less significant. Likewise, Bradford reviews on the literature of Claridge et al., finding that their kinetic data obtained over Al_2O_3-supported metals may illustrate a compensation effect. Where their data can be correlated by the following relationship between the apparent activation energy, *E*, and the pre-exponential factor, *A*:

$$ln\ A = \alpha + \frac{E}{R\theta} \quad (13)$$

where α is a constant, *R* is the gas constant, and θ is the isokinetic temperature. With their data, it was found that α ≈ 0 and θ = 940 ± 100 K so that

$$ln\ A\ (s^{-1}) \approx 0.54E\ (kcal/mol) \quad (14)$$

It is mentioned that such relationships are not uncommon, and a compensation effect has also been observed for the reverse reaction, CO hydrogenation to CH_4 [13].

2.5 Thermodynamic of Ethanol Dry Reforming

The conversion reactant in ethanol dry reforming is favoured at higher CO_2/EtOH ratios. This is proven by Sepideh, Nicolas and Francois [48] with the calculations of Delta Gibbs free energy DG for the global ethanol dry reforming reaction (Eq. 4) at equilibrium in a temperature range between 523 K and 1123 K. Their research shows that at temperatures below 523 K, DG was very small and, therefore, the reforming reaction rate was prohibitively low. Increased DG with temperature illustrated that equilibrium was attained faster at higher temperatures. It also shown that DG was increased at a higher CO_2/EtOH ratio.

Another interesting fact that was also proven by Sepideh, Nicholas and Francios is that for oxidant/EtOH molar ratios of 1:1, 2:1 and 3:1, carbon formation was thermodynamically unfavourable at temperatures above 1173, 1023 and 973 K, respectively. Calculation on H_2, CH_4, CO, CO_2 and carbon yields were done at equilibrium for different CO_2/EtOH ratio and it was theoretically found that H_2 yield increased at high temperatures. [48]

The same phenomenon is shown in Tsiakaras and Demin [49], to whom the study of solid oxide fuel cell (SOFC) are fed with ethanol and carbon dioxide reforming which are the thermodynamic equilibrium product. Equilibrium calculations were done within 800 K and 1200 K temperature range, and wherein carbon formation is thermodynamically unfavourable region was measured, assuming different oxidants/EtOH ratio of the initial system. It shows that the molar ratio of oxidant/EtOH, the carbon formed in the equilibrium mixture is thermodynamically impossible.

Selectivity under equilibrium conditions of methane with increasing temperature decreases. This theoretical observation also evidenced by the experimental data from Sun et al. [50], shown that the lower methane selectivity at higher temperatures is due to the steam and CO_2 reforming of methane rate becomes significant at higher temperatures. Dry reforming of methane decreased resulting in a higher rate of CO2 production temperature higher than 923 K, in agreement with CO2 yields calculated at equilibrium for this temperature range.

According to these theoretical calculations, the maximum CO_2 production is forecast at about 823 K. The reason to this is that the fact that the Boudouard reaction toward the production of carbon and CO_2 was advantageously carried out in the temperature range of 773–823 K. CO yield increased significantly at temperatures higher than 873 K. This is mainly due to the role of the Boudouard reaction is more important than the WGS of the CO generation, because water is present in the reaction in an amount much less than the carbon dioxide.

The influence of pressure on DRE was investigated by Wenju Wang and Yaquan [51] for the temperature range of 500–1500 K at a given CO_2/C_2H_5OH molar ratio of 1.0. The pressure from 0.1 to 2.0 MPa has no effect on the conversion of ethanol, which is already attained 100%. The increase of the pressure decreases the hydrogen yield and concentration. This can be ascribed to the increase of pressure shifting the equilibrium to CH4 and H2O which is attributed to methanation (Eq. (15) and (16)) and carbon formation (Eq. (17) and (18)), respectively.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (15)$$

$$CO2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (16)$$

$$CO + H_2 \rightarrow C + H_2O \quad (17)$$

$CO_2 + 2H_2 \rightarrow C + 2H_2O$ (18)

The influence of pressure on the yield and concentration of CO is shown in Fig. 5 (a) and (b). The increase of the pressure from 0.1 to 2.0 MPa does not change the CO concentration at temperatures of 500–700 K due to the domination of Eq. (1), whose overall molar numbers of the species do not change with the pressure. But at high temperatures, the increase of the pressure markedly decreases the CO concentration due to Eqs. (15) and (17).

Nitrogen was used as the inert component and the influence of it on DRE was investigated for the temperature range of 500–1500 K at a fixed carbon dioxide-to-ethanol molar ratio of 1.0 and 0.1 MPa. The increase of nitrogen-to-ethanol molar ratio from 0 to 100 has no effect on the conversion of ethanol, which is already attained 100%. However, nitrogen has a positive effect on the hydrogen yield. The increase of N_2/C_2H_5OH molar ratio from 0 to 100 slightly increases the CO yield as shown in Eq. (4), when the inert gas is added, the partial pressures of the reactants decrease, which favours H_2 and CO formation. [51]

2.6 Typical Catalytic System Used In Reforming

Compared to the early success of steam reforming [37], catalytic partial oxidation remained almost unexplored until 1990. Improving catalyst stability and performance for methane dry reforming was started to get focused by the end of 1993-1994. In 1990, Ashcroft et al. [38] tested lanthanide ruthenium oxides, as well as Ru supported on Al_2O_3 and pure RuO_2, at 1050 K and 1 atm. Conversion levels in excess of 90% and synthesis gas selectivities in the range 94–99% were reported. Diluting with nitrogen had a negative effect on conversion and synthesis gas selectivities. Vernon et al. [39] reported equilibrium yields over mixed oxides of Ni, Ru, Rh, Pd, Pt and Ir, or such transition metal catalysts supported on Al_2O_3. The effect of pressure (1–20 atm.) was investigated, and the catalyst performance (conversion and selectivity) was found to decrease with increasing pressure, which is to be expected from thermodynamics.

Cobalt catalysts were first studied by Choudhary et al. [40]. Different rare earth oxides (CeO_2, Nd_2O_2, Sm_2O_3, Yb_2O_3) were tested as supports and compared to the solid solution CoO–MgO. Based on the results, kinetically controlled formation of CO and H_2 was claimed.

Carbon deposition was found to proceed rapidly on some catalysts, probably influenced by the Boudouard reaction, but without degrading effects on conversion or selectivity. Carbon deposition on transition metals was reported by Claridge et al. [41], and the relative rates were in the order: Ni>Pd>Rh>Ru>Pt, Ir. The effect of calcination temperature was investigated by Wang and Ruckenstein [42], and the reducibility of observed species decreased in the sequence Co_3O_4 >Co_2AlO_4 >$CoAl_2O_4$.

The main reason for investigating other supports than alumina has been to avoid deactivation due to formation of $CoAl_2O_4$. Besides cobalt on alumina and CoO–MgO, there are numerous studies with cobalt supported on a wide range of supports. Alkaline earths, rare earths, SiO_2, TiO_2, Y_2O_3, ZrO_2, active carbon/graphite and Mayenite have been tested. One of the best supports has been shown to be oxidized diamond [43]. The cobalt catalysts typically gave lower conversion and synthesis gas selectivity as compared to the nickel catalysts. However, the addition of CoO, especially to NiO/ZrO_2 caused a dramatic reduction in the carbon deposition. No carbon formation was detected on the supported CoO catalysts. Nishimoto et al. [43] compared Co and Ni supported on oxidized diamond. No carbon deposition was observed over Co catalysts, while for Ni catalysts with 3 wt% Ni carbon was observed at temperatures below 923 K.

Due of the tendency of cobalt to oxidize, a promoter may be required to improve the reducibility at lower temperatures. Swaan et al. [44] tested Co/Al_2O_3 and Co/SiO_2, and compared the results to nickel on the same supports. It was found that the cobalt catalysts favored total combustion unless the reducibility of cobalt was promoted by adding a second metal, in this case Zn. However, the catalysts were not reduced before catalytic testing. Better reducibility and high yields of synthesis gas were reported by Mo et al. [45] when promoting Co/Al_2O_3 with Pt. While $CoAl_2O_4/Al_2O_3$ required high temperature reduction (1123 K, 1 h) to become active, promoting with 0.2 wt% Pt yielded higher conversion and synthesis gas selectivity when reduced at only 973 K. Adding more than 0.2 wt% Pt did not notably improve conversion or synthesis gas selectivity.

Whereas, there are also several catalytic system which have been studied previously for ethanol steam reforming. The performance of ceria supported Rh catalysts prepared with high and low surface areas for steam reforming and dry reforming of ethanol was investigated by Adriana M. da Silva and the co-researchers [52]. According to results of diffuse reflectance infrared Fourier transform spectroscopy of both reactions, dissociative adsorption of ethanol

over ceria gives rise to ethoxy species and bridging OH groups. Oxidation of ethoxy species proceeds by addition of O provided by the support from species such as Type II bridging O adatoms. Rh promotes demethanation of acetate to carbonate and the steam/dry reforming of CH_x species. Catalyst deactivation occurs from the deposition of carbon on the catalysts during both reactions. However, no carbon formation is observed on the Rh/CeO2 high surface area catalyst during steam reforming due to a higher surface fugacity of O from species adsorbed on the support that react to remove carbon.

Carbon and stainless steel as catalyst for the ethanol dry reforming process had also been studied by Spideh Jankhah and et al. [53] that it can be can be used efficiently as a catalytic precursor for ethanol cracking and dry reforming. His research was focused on the catalytic properties of carbon nano-filaments (CNF), as produced through the catalytic dry reforming of ethanol, using low-carbon steel as the catalyst. It has been quantitatively demonstrated that these carbon nano-filaments have high catalytic activity in respect of the ethanol dry reforming and cracking reactions. Iron carbide particles, encapsulated in the CNF, are shown to be the active agents possessing the observed catalytic properties. Thermodynamic equilibrium analysis and experimental data on thermal and catalytic ethanol cracking and dry reforming reactions at various CO2/ethanol ratios were also studied by this team of researcher in another paper. [48] Both thermodynamic analysis and the experimental results with a carbon steel catalyst precursor revealed that the highest hydrogen and carbon yields were obtained at 823 K. It was also found that carbon steel was an active catalyst for ethanol cracking at 823 K and that thermal cracking and thermal reforming of ethanol were not favoured under these operating conditions. In both catalytic dry reforming and cracking of ethanol, carbon deposits were in the form of carbon nano-filaments.

Jorge D.A. Belleido et al. [54] investigated the performance of supported nickel catalysts of composition $Ni/Y_2O_3–ZrO_2$ that were synthesized in one step by the polymerization method and compared with a nickel catalyst prepared by wet impregnation. Stronger interactions were observed in the formed catalysts between NiO species and the oxygen vacancies of the $Y_2O_3–ZrO_2$ in the catalysts made by polymerization, and these were attributed to less agglomeration of the NiO during the synthesis of the catalysts in one step. The dry reforming of ethanol was catalyzed with a maximum CO_2 conversion of 61% on the 5NiYZ catalyst at 1073 K, representing a better response than for the catalyst of the same composition prepared by wet impregnation.

Rhodium, Rh one of the popular active metal catalyst studied for its excellent catalytic activities in various reforming technologies of many hydrocarbon compounds due to the fact that Rh possessed the greatest capacity toward C–C bond cleavage. Various M_xO_y–Al_2O_3 oxides (M = Zr, Mg, Ni, Ce, La), prepared by a sol–gel method as supports for rhodium catalysts in methane and ethanol dry reforming was experimented by Asmaa Drif et al. [54]. After calcination, the Rh/M_xO_y–Al_2O_3 catalysts present BET surface areas between 85 and 208 m^2g^{-1}. It was found that the performance of Rh catalysts in hydrogen yield lied in the ranking of Rh/NiO–Al_2O_3 > Rh/Al_2O_3 > Rh/MgO–Al_2O_3 ≈ Rh/CeO_2–Al_2O_3 > Rh/ZrO_2–Al_2O_3 > Rh/La_2O_3–Al_2O_3 for methane dry reforming. Likewise, ethanol dry reforming at 1073K showed similarities with the ranking Rh/NiO–Al_2O_3 >> Rh/Al_2O_3 ≈ Rh/MgO–Al_2O_3 ≈ Rh/CeO_2–Al_2O_3 > Rh/ZrO_2–Al_2O_3 ≈ Rh/La_2O_3–Al_2O_3. For the two reactions, the best catalyst is Rh/NiO–Al_2O_3 even if it deactivates during the reaction due to carbon deposition. This high activity may be explained by both the presence of the $NiAl_2O_4$ spinel phase, avoiding the deactivation of rhodium by migration in alumina, and the high dispersion of Rh favoured by the presence of nickel particles at the support surface. Moreover, Ni particles on the support surface also contribute to the activity as demonstrated by the high hydrogen yield obtained in the presence of NiO–Al_2O_3, which is similar to the one obtained with Rh/Al_2O_3. [54]

2.7 Promoter

One way to avoid the formation of carbon deposition is the addition of promoter such as the alkaline and earth alkaline metals [55, 56]. The promoter can migrate from the support to the metal particles surface, deactivating sites where methane decomposition takes place (reaction (2)), by oxidizing carbon formation to form carbon monoxide, and/or the promoter can catalyze the CO2 gasification of the carbon formed during reaction (reverse of reaction (3)) [56, 57]. Even if the promoter is able to avoid carbon deposition; the partial coverage of cobalt active metal by low promoter content caused the relatively small decrease of the catalytic activity while the higher promoter content could lose the catalytic activity due to the coverage of cobalt active site and generating larger particle size. Some detailed studies have shown that additives like potassium, lanthanum and cerium preferentially bind to the step sites working as the coking sites and, hence, suppress graphite formation, without significantly influencing the catalytic activity for the reforming [60]. The addition of potassium and strontium as promoter

could prevent the catalyst from carbon deposition [60]. The potassium promoted catalyst gives a lower carbon deposit compared to strontium in similar catalytic activity result indicating that potassium is a more effective promoter than strontium. However, the potassium promoter showed a larger particle sizes of metal phase on the support because of the agglomeration of cobalt metal over the support. The results clearly show that potassium addition did not lead to stabilization of Co centers on the support and cannot prevent metal sintering [61].

By small doped of lanthanum as promoter in zirconium oxide supported catalyst, the stable and coke resistant catalyst was found because of the high and homogeneous dispersion of small sized metal promoter to the support [61]. The addition of lanthanum promoter enhances the surface area and the thermal stability of ZrO_2 by stabilizing the tetragonal phase of zirconia [63].

Ceria, is the another kind of promoter studied to enhance the performance of catalyst [61].Ceria is known to be a material with high oxygen storage capacity, which can be combined with other solid materials such as ZrO_2 to obtain a catalytic surface that promotes the formation of oxygen vacancies and increases the mobility of oxygen through the lattice [63]. The presence of ceria on the surface creates an additional storage capacity for oxygen coming from ZrO_2 support; it goes through continuous reduction/oxidation cycle during the reaction producing mobile surface oxygen, and enhances the oxygen transfer, all of which makes the active metal more resistant to carbon deposition.

It is also well known that small amounts of noble metals can promote the reducibility of the base metal and stabilize the reduced state during the catalytic process [64, 65]. Platinum and ruthenium were known capable to reduce the oxidation of metal which is caused by the synergetic effect of cobalt and noble metal. By addition of noble metal promoter, the number of cobalt oxides interacting strongly with support was decreased and the reduction temperature are shifted lower. In most cases, platinum improved the catalytic stability more efficiently than the double amount of ruthenium [66, 67].